



(12) **EUROPEAN PATENT SPECIFICATION**

- (45) Date of publication and mention of the grant of the patent:  
**02.04.2003 Bulletin 2003/14**
- (51) Int Cl.7: **C07F 17/00**, C08F 110/06,  
C08F 4/622
- (21) Application number: **99964560.9**
- (86) International application number:  
**PCT/EP99/09855**
- (22) Date of filing: **13.12.1999**
- (87) International publication number:  
**WO 00/035929 (22.06.2000 Gazette 2000/25)**

(54) **BIMETALLIC METALLOCENE CATALYST FOR ISOTACTIC POLYPROPYLENE POLYMERISATION**

BIMETALLISCHES-METALLOCENE KATALYSATORSYSTEM FÜR ISOTACTISCHE POLYPROPYLEN-POLYMERISATION

CATALYSEUR METALLOCENE BIMETALLIQUE DE LA POLYMERISATION DE POLYPROPYLENES ISOTACTIQUES

- (84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE**
- (30) Priority: **14.12.1998 EP 98123747**
- (43) Date of publication of application:  
**14.11.2001 Bulletin 2001/46**
- (73) Proprietor: **ATOFINA Research**  
**7181 Seneffe (Feluy) (BE)**
- (72) Inventors:  
• **RAZAVI, Abbas**  
**B-7000 Mons (BE)**  
• **MISERQUE, Olivier**  
**B-1490 Court-Saint-Etienne (BE)**
- (56) References cited:  
**EP-A- 0 416 815**                      **WO-A-98/27103**
- **CHEN ET AL: "Constrained Geometry Dialkyl Catalysts. Efficient Syntheses, C-H Bond Activation Chemistry, Monomer-Dimer Equilibration, and.alpha.-Olefin Polymerization Catalysis"**  
**ORGANOMETALLICS,US,WASHINGTON, DC, vol. 16, no. 16, 1 January 1997 (1997-01-01), pages 3649-3657, XP002080367 ISSN: 0276-7333**
  - **CHEMICAL ABSTRACTS, vol. 125, no. 15, 7 October 1996 (1996-10-07) Columbus, Ohio, US; abstract no. 195895, KRUT'KO, D. P. ET AL: "Tetramethyl(2-methylthioethyl)cyclopentadienyl complexes of zirconium(IV). Synthesis, crystal structure, and dynamic behavior in solutions" XP002133563 & IZV. AKAD. NAUK, SER. KHIM. (1996), (4), 984-992 ,**
  - **HUGHES A K ET AL: "EFFICIENT NEW SYNTHETIC ROUTE TO BIDENTATE, MONOMERIC CYCLOPENTADIENYL-AMIDE COMPLEXES OF GROUP 4 TRANSITION METALS: SYNTHESIS AND CHARACTERIZATION OF THE ZIRCONIUM AND HAFNIUM COMPLEXES**  
**Uän5:SIGMA-C5H4(CH2)3NMEüMX2(NHME2) (X = CL, I, M = ZR;X = I, M = HF) AND Uän5:SIGMA-C5H4(CH2)3NMEüZRX2 (X = NME2"**  
**ORGANOMETALLICS,US,WASHINGTON, DC, vol. 12, no. 5, 1 March 1993 (1993-03-01), pages 1936-1945, XP000575406 ISSN: 0276-7333**
  - **KRUT'KO, DMITRII P. ET AL: "(2-Diphenylphosphinoethyl)cyclopentadieny I complexes of zirconium (IV): synthesis, crystal structure and dynamic behavior in solutions" POLYHEDRON (1998), 17(22), 3889-3901 , XP000889781**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

- **VAN DER ZEIJDEN, ADOLPHUS A. H. ET AL:**  
**"Synthesis and Characterization of**  
**Monocyclopentadienyl Titanium and Zirconium**  
**Complexes Bearing a Chelating (Chiral) Ether**  
**Side Chain on the Cp Ring"**  
**ORGANOMETALLICS (1997), 16(12), 2651-2658 ,**  
**XP000889678**

## Description

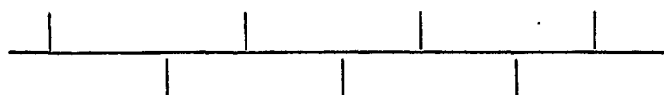
**[0001]** The present invention relates to a metallocene catalyst component for use in preparing isotactic polyolefins, especially polypropylenes. The invention further relates to a catalyst system which incorporates the metallocene catalyst component and a process for preparing such isotactic polyolefins.

**[0002]** Olefins having 3 or more carbon atoms can be polymerised to produce a polymer with an isotactic stereochemical configuration. For example, in the polymerisation of propylene to form polypropylene, the isotactic structure is typically described as having methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer. This can be described using the Fischer projection formula as follows:



**[0003]** Another way of describing the structure is through the use of NMR spectroscopy. Bovey's NMR nomenclature for an isotactic pentad is ... mmmm with each "m" representing a "meso" diad or successive methyl groups on the same side in the plane.

**[0004]** In contrast to the isotactic structure, syndiotactic polymers are those in which the methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer. Using the Fischer projection formula, the structure of a syndiotactic polymer is described as follows:



**[0005]** In NMR nomenclature, a syndiotactic pentad is described as ... rrrr... in which "r" represents a "racemic" diad with successive methyl groups on alternate sides of the plane.

**[0006]** In contrast to isotactic and syndiotactic polymers, an atactic polymer exhibits no regular order of repeating unit. Unlike syndiotactic or isotactic polymers, an atactic polymer is not crystalline and forms essentially a waxy product.

**[0007]** WO96/0073 relates to "constrained geometry" complexes which are said to be useful as catalysts in the production of polyethylene. Some of the constrained geometry metallocenes according to WO96/00734 have a bridge between the cyclopentadienyl ring and the metal which includes a divalent heteroatom ligand. These constrained geometry metallocenes are not reported for production of polypropylenes.

**[0008]** In Polymer Preprints 37(2), p474 of 1996, McKnight *et al* report that some Group IV mono-cyclopentadienyl amido complexes may be used as catalysts in the production of polypropylene but that the polymer product is almost completely atactic.

**[0009]** In Polyhedron, (1998), 17, pp 3889-3901 D. Krut'ko *et al.* disclose constrained geometry zirconium (IV) complexes, which may be monomeric or dimeric. Similar zirconium (IV) complexes are disclosed in Organometallics, (1997), 16, 2651-2658 by A. van der Zeijden *et al.*

**[0010]** Published US patent specification US 5,808,122 discloses organometallic catalysts for olefin polymerisation. These catalysts comprise metallocenes of chromium, molybdenum and tungsten having cyclopentadienyl ligands bridged to heteroatom ligands.

**[0011]** In Organometallics, (1996), 15(11), 2668, D. Carpeaetti *et al.* disclose the dimeric compound,  $\{[(C_5H_4)-SiMe_2(N-t-Bu)]ZrCl(\mu-Cl)\}_2$ , and its monomeric counterpart.

**[0012]** In Organometallics, (1993), 12, 1936-1945, A. Hughes *et al.* disclose monomeric constrained geometry metallocene complexes that may have some catalytic activity.

**[0013]** In EP 0 416 815 and the related EP 0 764 653 constrained geometry catalysts for addition polymerisation of bulky olefins are disclosed. These catalysts may comprise monomers and dimers of metallocenes having a Cp ring attached to a metal centre and having a bridge to a heteroatom which is also bound to the metal centre.

**[0014]** WO 92/05204 and the related patent application, WO 95/00562, disclose methods of producing crystalline polyolefins using constrained geometry metallocenes. A wide variety of such metallocenes is disclosed, including dimeric and monomeric metallocenes.

[0015] WO 98/27103 discloses a polymerisation process which employs fused ring substituted indenyl metal complexes. A wide variety of complexes are disclosed, all of which are monomeric.

[0016] In contrast, the present applicants have surprisingly found that isotactic polypropylene may be produced using constrained geometry metallocene catalysts, especially from a novel class of dimeric metallocene compounds.

[0017] In a first aspect, the present invention provides a metallocene compound having the general formula: CpAXMQ<sub>1</sub>Q<sub>2</sub>Cp'A'X'M'Q<sub>1</sub>'Q<sub>2</sub>' wherein Cp and Cp' are each independently a substituted or unsubstituted indenyl moiety; M and M' are each independently a metal chosen from Group IV B transition metals and vanadium, and coordinate to Cp and Cp' respectively; X and X' are each independently a substituted or unsubstituted Group VA or VIA' heteroatom and coordinate to M and M' respectively; A and A' are bridging groups between Cp and X and between Cp' and X' respectively and are independently chosen from -SiR'<sub>2</sub>-O-SiR'<sub>2</sub>-, -Si<sub>n</sub>R'<sub>m</sub>-, -C<sub>n</sub>R'<sub>m</sub>- and -CR'<sub>2</sub>-SiR'<sub>2</sub>-CR'<sub>2</sub>-SiR'<sub>2</sub>-, in which each R' is independently H or hydrocarbyl having 1 to 20 carbon atoms, n is an integer in the range 1 to 4 and m=2n; each Q<sub>1</sub>, Q<sub>2</sub> and Q<sub>1</sub>' and Q<sub>2</sub>' is independently a coordinating group which is hydrogen, halogen or hydrocarbyl having 1 to 20 carbon atoms and each of Q and Q<sub>1</sub>' is coordinated to both M and M'.

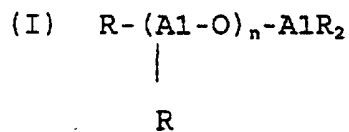
[0018] Preferably, at least one of Cp and Cp' is substituted.

[0019] The metallocene compound preferably has a dimeric structure and preferably also has an active site with local C<sub>2</sub> symmetry.

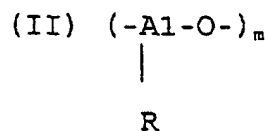
[0020] The metallocene may be used as a catalyst component for the production of a polyolefin, especially isotactic polypropylene.

[0021] In a further aspect, the present invention provides a catalyst system or use in preparing polyolefins which comprises (a) a metallocene compound as defined above; and (b) an aluminium- or boron-containing cocatalyst capable of activating the metallocene compound. Suitable aluminium-containing cocatalysts comprise an alumoxane, an alkyl aluminium and/or a Lewis acid.

[0022] The alumoxanes usable in the process of the present invention are well known and preferably comprise oligomeric linear and/or cyclic alkyl alumoxanes represented by the formula:



for oligomeric, linear alumoxanes and



for oligomeric, cyclic alumoxane,

wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C<sub>1</sub>-C<sub>8</sub> alkyl group and preferably methyl. Generally, in the preparation of alumoxanes from, for example, aluminium trimethyl and water, a mixture of linear and cyclic compounds is obtained.

[0023] Suitable boron-containing cocatalysts may comprise a triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696, or those of the general formula [L'-H]<sup>+</sup> [B Ar<sub>1</sub> Ar<sub>2</sub> X<sub>3</sub> X<sub>4</sub>]<sup>-</sup> as described in EP-A-0277004 (page 6, line 30 to page 7, line 7).

[0024] The catalyst system may be employed in a solution polymerisation process, which is homogeneous, or a slurry process, which is heterogeneous. In a solution process, typical solvents include hydrocarbons with 4 to 7 carbon atoms such as heptane, toluene or cyclohexane. In a slurry process it is necessary to immobilise the catalyst system on an inert support, particularly a porous solid support such as talc, inorganic oxides and resinous support materials such as polyolefin. Preferably, the support material is an inorganic oxide in its finely divided form.

[0025] Suitable inorganic oxide materials which are desirably employed in accordance with this invention include Group 2a, 3a, 4a or 4b metal oxides such as silica, alumina and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins such as finely divided polyethylene.

[0026] Preferably, the support is a silica having a surface area comprised between 200 and 900 m<sup>2</sup>/g and a pore volume comprised between 0.5 and 4 ml/g.

[0027] The amount of alumoxane and metallocenes usefully employed in the preparation of the solid support catalyst can vary over a wide range. Preferably the aluminium to transition metal mole ratio is in the range between 1:1 and 100:1, preferably in the range 5:1 and 50:1.

[0028] The order of addition of the metallocenes and alumoxane to the support material can vary. In accordance with a preferred embodiment of the present invention alumoxane dissolved in a suitable inert hydrocarbon solvent is added to the support material slurried in the same or other suitable hydrocarbon liquid and thereafter a mixture of the metallocene catalyst component is added to the slurry.

[0029] Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperature and which do not react with the individual ingredients. Illustrative examples of the useful solvents include the alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane, and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene.

[0030] Preferably the support material is slurried in toluene and the metallocene and alumoxane are dissolved in toluene prior to addition to the support material.

[0031] Without wishing to be bound by any theory, it is possible that the dimeric metallocene compounds described above may, in use, form corresponding monomeric compounds which act as the active catalytic species. Accordingly, the dimeric compounds may be precursors for active monomeric compounds.

[0032] In a further aspect, the present invention provides a process for preparing polyolefins, particularly isotactic polypropylenes, which comprises contacting the catalyst system with at least one olefin in a reaction zone under polymerisation conditions. The olefin is preferably propylene.

[0033] In a further aspect, the present invention provides use of a catalyst comprising a metallocene compound for the production of isotactic polypropylene, wherein the metallocene compound has the general formula CpAXMQ<sub>2</sub>, in which Cp is a cyclopentadienyl moiety substituted so that when in use isotactic polypropylene is produced; M is a metal chosen from Group IVB transition metals and vanadium, and coordinates to Cp; X is a substituted or unsubstituted Group VA or VIA heteroatom which coordinates to M; A is a bridging group between Cp and X which is chosen from -SiR'<sub>2</sub>-O-SiR'<sub>2</sub>-, -Si<sub>n</sub>R'<sub>m</sub>-, -C<sub>n</sub>R'<sub>m</sub>-, -CR'<sub>2</sub>-SiR'<sub>2</sub>-CR'<sub>2</sub>-SiR'<sub>2</sub>-, in which each R' is independently H or hydrocarbyl having 1 to 20 carbon atoms, n is an integer in the range 1 to 4 and m=2n; and each Q is independently hydrogen, halogen or hydrocarbyl having 1 to 20 carbon atoms. The metallocene compound preferably has an active site with local C1 symmetry when the active catalyst is in the form of a monomer.

[0034] Preferably, each cyclopentadienyl moiety is a substituted or unsubstituted indenyl, more preferably a substituted or unsubstituted benzoindenyl. A preferred substitution position is position 2 in the cyclopentadienyl ring, the substituent of which may be hydrocarbyl having 1 to 20 carbon atoms, such as methyl.

[0035] M is preferably Zr.

[0036] Each heteroatom is preferably nitrogen, phosphorus, oxygen or sulphur so as to provide a suitable divalent ligand for constraining the geometry of the metallocene. The heteroatom is typically substituted with H, hydrocarbyl having 1 to 20 carbon atoms or silyl and is preferably nitrogen. Each A and A' is preferably SiR'<sub>2</sub> wherein each R' is preferably methyl.

[0037] In a further aspect of the invention, there is provided use of a metallocene compound as described above wherein the metallocene compound is formed from a dimeric metallocene compound also as described above.

[0038] The invention will now be described in further detail, by way of example only, with reference to the following Examples and accompanying drawings, in which:

FIGURE 1 shows the results of crystal structure analysis for (Me<sub>2</sub>Si(tbuN)(2-MeBenzInd)ZrCl<sub>2</sub>)<sub>2</sub>;

FIGURE 2 shows a <sup>13</sup>C NMR spectrum of polypropylene produced in accordance with the present invention; and

FIGURE 3 shows the results of differential scanning calorimetry on the polypropylene.

#### Example 1: Preparation of the dimer of (t-butylamido)(2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilane zirconium dichloride:

1. (2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilyl-t-butylamine

[0039] A solution of 83.2 mmol of 2-methyl-4,5-benzoindene in 150 cc of diethylether was added dropwise at room temperature to a solution of 83.0 mmol of dichlorodimethylsilane in 100 cc of diethylether. The mixture was stirred overnight at room temperature and then transferred on a solution of 83.0 mmol of t-butylamidolithium in 300 cc of diethylether. After the mixture has been stirred for 8 hours, the precipitated lithium chloride was eliminated by filtration. The solution was concentrated under vacuum and 250 cc of n-pentane were added to the residue. The brown solid which precipitated after 1 hour at 20°C was filtered off and dried under an oil-pump vacuum. 20.6g (80%) of (t-butyla-

mido)(2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilane were obtained.

2. Preparation of dilithio salt, (2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilyl-t-butylamide:

5 [0040] 10.0 g (32.3 mmol) of (t-butylamido) (2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilane were dissolved in 200 cc of diethylether and 40.4 cc (64.6 mmol) of 1.6 molar diethylether solution of methylolithium were added dropwise at room temperature. After the mixture has been stirred overnight, the solvent was removed under vacuum. The brown residue was washed several times with n-pentane and dried under vacuum. 11.9 g of the dilithio salt were obtained as a brown powder.

10

3. Preparation of (2-methyl-4,5-benzo-inden-1-yl)-1,1-dimethylsilyl-t-butylamido zirconium dichloride:

15 [0041] 11.9 g of the dilithio salt was suspended in 200 cc of pentane and 7.6 g (32.6 mmol) of zirconium tetrachloride were added in small portions. The mixture was stirred for 10 hours at room temperature. The resulting yellow solid was filtered off, washed several times with n-pentane and dried under vacuum. The solid was suspended in 500 cc of n-hexane and heated under reflux for 1 hour. The yellow solid was then eliminated by filtration at 50°C and the filtrate concentrated under vacuum. 1.9 g (12%) of (t-butylamido) (2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilane zirconium dichloride were obtained as the dimer structure determined by X-ray diffraction analysis (yellow crystals were obtained by recrystallization in dichloromethane). 1H NMR spectrum (300 MHz, CD<sub>2</sub>C<sub>12</sub>, d in ppm): 8.09-7.37 (m, 7H, 2-MebenzInd-H), 2.43 (s, 3H, 2-CH<sub>3</sub>-benzInd), 1.31 (s, 9H, t-BuN), 0.87 and 0.71 (s, 3H, Me<sub>2</sub>Si).

20

**Example 2: Preparation of the dimer of (t-butylamido)(2-methyl-4,5-benzoinden-1-yl)-1,1-dimethylsilane titanium dichloride:**

25 [0042] The procedure described in Example I was repeated with TiCl<sub>4</sub> being used instead of ZrCl<sub>4</sub>. 1H NMR spectrum (300 MHz, CD<sub>2</sub>C<sub>12</sub>, d in ppm): 8.08-7.32 (m, 7H, 2-MebenzInd-H), 2.47 (s, 3H, 2-CH<sub>3</sub>-benzInd), 1.48 (s, 9H, t-BuN), 0.98 and 0.84 (s, 3H, Me<sub>2</sub>Si).

30

**Example 3: Polymerisation procedures**

35

[0043] Each polymerisation was performed in a 4 litre bench reactor with pure polypropylene or with diluent such as cyclohexane or isobutane with the quantities reported in the following Tables. Polymerisation was initiated by introducing metallocene (1 to 10 mg) precontacted with 1 ml of MAO (methylaluminumoxane) (30% solution in toluene obtained from WITCO) three minutes prior to its introduction into the reactor.

40

[0044] Table 1 shows the results of polypropylene production using the catalyst of Example 1 in an amount of 2.8mg in 2l diluent with 850ppm cocatalyst. A polymer with a high melting point is obtained in the form of a crystalline powder. 13C NMR analysis confirms that the polypropylene is isotactic and Table 2 shows the pentad intensity distribution thereof. A high mmmm pentad intensity of 87% is observed with mm triads of 93% and m dyads of 95.5%. These results are comparable to those obtained with polypropylenes made using highly stereoselective stereorigid classical metallocene based catalysts. The relatively low occurrence of 2-1 and 1-3 regiodefects is very surprising. The high stereoregularity of the polymer explains the high melting point observed.

45

[0045] Figure 2 shows a 13C NMR spectrum of the polymer and Figure 3 shows a HNMR spectrum of the metallocene in CO<sub>2</sub>Cl<sub>2</sub> at 25°C.

50

55

Table 1 - Polymerization with  $(Me_2Si(tBuN)(2-MeBenzInd)ZrCl_2)_2$ 

Pol. Temp (°C)	Residence time (mins)	Mn (Da)	Mw (Da)	Mz (Da)	D	D'	Melt. Temp (°C)
60	60	60,900	259,800	704,000	4.3	2.7	146.9

Key:  $MI_2$  = Melt index; Mn = number average molecular weight; Mw = weight average molecular weight  
 $D = Mw/Mn$ ;  $D' = Mz/Mw$

Table 2 -

Microtacticity with (Me <sub>2</sub> Si('buN)(2-MeBenzInd)ZrCl <sub>2</sub> )	
<b>PENTADS</b>	
Sequence	%
mmmm	86.93
mmmr	4.94
rmmr	1.14
mmrr	3.66
rmrr+mrmm	0.64
mrmr	0.60
rrrr	0.39
mrrr	0.41
mrrm	1.29
<b>TRIADS</b>	
Sequence	%
mm	93.01
mr	4.90
rr	2.09
<b>DYADS</b>	
Sequence	%
m	95.46
r	4.54
<b>Misinsertions</b>	
	<b>mole %</b>
2,1	0.33
1,3	0.00

## Claims

1. A metallocene compound having the general formula: CpAXMQ<sub>1</sub>Q<sub>2</sub>Cp'A'X'M'Q<sub>1</sub>'Q<sub>2</sub>' wherein Cp and Cp' are each independently a substituted or unsubstituted indenyl moiety; M and M' are each independently a metal chosen from Group IV B transition metals and vanadium, and coordinate to Cp and Cp' respectively; X and X' are each independently a substituted or unsubstituted Group VA or VIA heteroatom and coordinate to M and M' respectively; A and A' are bridging groups between Cp and X and between Cp' and X' respectively and are independently chosen from -SiR'<sub>2</sub>-O-SiR'<sub>2</sub>-, -Si<sub>n</sub>R'<sub>m</sub>-, -C<sub>n</sub>R'<sub>m</sub>- and -CR'<sub>2</sub>-SiR'<sub>2</sub>-CR'<sub>2</sub>-SiR'<sub>2</sub>-, in which each R' is independently H or hydrocarbyl having 1 to 20 carbon atoms, n is an integer in the range 1 to 4 and m=2n; each Q<sub>1</sub>, Q<sub>2</sub> and Q<sub>1</sub>' and Q<sub>2</sub>' is independently a coordinating group which is hydrogen, halogen or hydrocarbyl having 1 to 20 carbon atoms and each of Q<sub>1</sub> and Q<sub>1</sub>' is coordinated to both M and M'.
2. A metallocene compound according to claim 1, wherein each indenyl moiety is substituted or unsubstituted benzindenyl.
3. A metallocene compound according to claim 1 or claim 2, wherein the indenyl moiety is substituted at position 2 with a hydrocarbyl having 1 to 20 carbon atoms.



## EP 1 153 032 B1

4. A metallocene compound according to any one of the preceding claims, wherein the metal is Zr.
5. A metallocene compound according to any one of the preceding claims, wherein the heteroatom is nitrogen, phosphorus, oxygen or sulphur and is substituted with H, hydrocarbyl having 1 to 20 carbon atoms or silyl.
6. A metallocene compound according to claim 5, wherein the heteroatom is nitrogen.
7. A metallocene compound according to any one of the preceding claims, wherein each A and A' is SiR'<sub>2</sub>.
8. A metallocene compound according to claim 7, wherein each R' is methyl.
9. A metallocene compound according to any one of the preceding claims, whose active site has local C<sub>2</sub> symmetry.
10. A metallocene compound according to any one of the preceding claims, which has a dimeric structure.
11. A metallocene compound according to any one of the preceding claims, comprising (t-butylamido)(2-methyl-4,5-benzindolen-1-yl)-1,1-dimethyl silane zirconium chloride or (t-butylamido)(2-methyl-4,5-benzindolen-1-yl)-1,1-dimethyl silane titanium chloride.
12. A catalyst system for use in preparing polyolefins, which comprises (a) a metallocene compound as defined in any one of the preceding claims; and (b) an aluminium- or boron-containing cocatalyst capable of activating the metallocene compound.
13. A catalyst system according to claim 12, which further comprises an inert support.
14. Use of a metallocene compound, or a catalyst system, as defined in any one of the preceding claims, as a catalyst component for the production of a polyolefin.
15. Use according to any of claims claim 12-14, wherein the polyolefin comprises isotactic polypropylene.
16. A process for preparing polyolefins, which comprises contacting a catalyst system as defined in claim 12 or claim 13 with at least one olefin in a reaction zone under polymerisation conditions.
17. A process according to claim 16, wherein the olefin is propylene and the polyolefin is isotactic polypropylene.
18. Use of a metallocene compound as a catalyst component for the production of isotactic polypropylene, wherein the metallocene compound comprises a metallocene having the general formula : CpAXMQ<sub>1</sub>Q<sub>2</sub>Cp'A'X'M'Q<sub>1</sub>'Q<sub>2</sub>' wherein Cp and Cp' are each independently a substituted or unsubstituted cyclopentadienyl moiety; M and M' are each independently a metal chosen from Group IV B transition metals and vanadium, and coordinate to Cp and Cp' respectively; X and X' are each independently a substituted or unsubstituted Group VA or VIA heteroatom and coordinate to M and M' respectively; A and A' are bridging groups between Cp and X and between Cp' and X' respectively and are independently chosen from -SiR'<sub>2</sub>-O-SiR'<sub>2</sub>-, -Si<sub>n</sub>R'<sub>m</sub>-, -C<sub>n</sub>R'<sub>m</sub>- and -CR'<sub>2</sub>-SiR'<sub>2</sub>-CR'<sub>2</sub>-SiR'<sub>2</sub>-, in which each R' is independently H or hydrocarbyl having 1 to 20 carbon atoms, n is an integer in the range 1 to 4 and m=2n; each Q<sub>1</sub>, Q<sub>2</sub> and Q<sub>1</sub>' and Q<sub>2</sub>' is independently a coordinating group which is hydrogen, halogen or hydrocarbyl having 1 to 20 carbon atoms and each of Q<sub>1</sub> and Q<sub>1</sub>' is coordinated to both M and M'.
19. Use according to claim 18, wherein the metallocene compound comprises a compound as defined in any of claims 1-11.
20. Use of a catalyst system for preparing isotactic polypropylene, which system comprises (a) a metallocene compound as defined in claim 18 or claim 19; and (b) an aluminium- or boron-containing cocatalyst capable of activating the metallocene compound.
21. A process for preparing isotactic polypropylene, which comprises contacting a catalyst system as defined in claim 20 with propylene in a reaction zone under polymerisation conditions.
22. Use of a catalyst comprising a metallocene compound for the production of isotactic polypropylene, wherein the metallocene compound has the general formula CpAXMQ<sub>2</sub>, in which Cp is a cyclopentadienyl moiety substituted;

M is a metal chosen from Group IVB transition metals and vanadium, and coordinates to Cp; X is a substituted or unsubstituted Group VA or VIA heteroatom which coordinates to M; A is a bridging group between Cp and X which is chosen from  $-\text{SiR}'_2\text{-O-SiR}'_2-$ ,  $-\text{Si}_n\text{R}'_m-$ ,  $-\text{C}_n\text{R}'_m-$  and  $-\text{CR}'_2\text{-SiR}'_2\text{-CR}'_2\text{-SiR}'_2-$ , in which each R is independently H or hydrocarbyl having 1 to 20 carbon atoms, n is an integer in the range 1 to 4 and  $m=2n$ ; and each Q is independently hydrogen, halogen or hydrocarbyl having 1 to 20 carbon atoms.

- 5
23. Use according to claim 22, wherein the cyclopentadienyl moiety is a substituted indenyl.
- 10
24. Use according to claim 23, wherein the substituted indenyl moiety is substituted benzoindenyl.
25. Use according to any one of claims 22 to 24, wherein the cyclopentadienyl moiety is substituted at position 2.
- 15
26. Use according to claim 25, wherein the cyclopentadienyl moiety is substituted with a hydrocarbyl having 1 to 20 carbon atoms.
27. Use according to any one of claims 22 to 26, wherein the metal is Zr.
28. Use according to any one of claims 22 to 27, wherein the heteroatom is nitrogen, phosphorus, oxygen or sulphur and is substituted with H, hydrocarbyl having 1 to 20 carbon atoms or silyl.
- 20
29. Use according to claim 28, wherein the heteroatom is nitrogen.
30. Use according to any one of claims 22 to 29, wherein A is  $\text{SiR}'_2$ .
- 25
31. Use according to claim 30, wherein each R' is methyl.
32. Use according to any one of claims 22 to 31, wherein the catalyst further comprises an aluminium- or boron-containing cocatalyst capable of activating the metallocene compound.
- 30
33. Use according to any one of claims 22 to 32, wherein the metallocene compound is formed from a metallocene compound as defined in any one of claims 1 to 11.

### Patentansprüche

- 35
1. Metallocenverbindung mit der allgemeinen Formel:  $\text{CpAXMQ}_1\text{Q}_2\text{Cp}'\text{A}'\text{X}'\text{M}'\text{Q}'_1\text{Q}'_2$ , wobei Cp und Cp' jeweils unabhängig ein substituierter oder unsubstituierter Indenylrest sind; M und M' sind jeweils unabhängig ein Metall, ausgewählt aus Gruppe IV B Übergangsmetallen und Vanadium und koordinieren an Cp bzw. Cp'; X und X' sind jeweils unabhängig ein substituiertes oder unsubstituiertes Gruppe VA oder VIA Heteroatom und koordinieren an M bzw. M'; A und A' sind Verbrückungsgruppen zwischen Cp und X und zwischen Cp' und X' und sind unabhängig aus  $-\text{SiR}'_2\text{-O-SiR}'_2-$ ,  $-\text{Si}_n\text{R}'_m-$ ,  $-\text{C}_n\text{R}'_m-$  und  $-\text{CR}'_2\text{-SiR}'_2\text{-CR}'_2\text{-SiR}'_2-$  ausgewählt, wobei jedes R' unabhängig H oder Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen ist, n ist eine ganze Zahl in dem Bereich von 1 bis 4, und  $m=2n$ ; jedes  $\text{Q}_1$ ,  $\text{Q}_2$  und  $\text{Q}'_1$  und  $\text{Q}'_2$  ist unabhängig eine Koordinierungsgruppe, die Wasserstoff, Halogen oder Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen ist, und jedes  $\text{Q}_1$  und  $\text{Q}'_1$  ist an beide M und M' koordiniert.
- 40
2. Metallocenverbindung nach Anspruch 1, wobei jeder Indenylrest substituiertes oder unsubstituiertes Benzoindenyl ist.
3. Metallocenverbindung nach Anspruch 1 oder Anspruch 2, wobei der Indenylrest an Position 2 mit einem Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen substituiert ist.
- 50
4. Metallocenverbindung nach einem der vorhergehenden Ansprüche, wobei das Metall Zr ist.
5. Metallocenverbindung nach einem der vorhergehenden Ansprüche, wobei das Heteroatom Stickstoff, Phosphor, Sauerstoff oder Schwefel ist und mit H, Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen oder Silyl substituiert ist.
- 55
6. Metallocenverbindung nach Anspruch 5, wobei das Heteroatom Stickstoff ist.

## EP 1 153 032 B1

7. Metallocenverbindung nach einem der vorhergehenden Ansprüche, wobei jedes A und A'  $\text{SiR}'_2$  ist.
8. Metallocenverbindung nach Anspruch 7, wobei jedes R' Methyl ist.
- 5 9. Metallocenverbindung nach einem der vorhergehenden Ansprüche, deren aktive Stelle lokale C<sub>2</sub> Symmetrie hat.
10. Metallocenverbindung nach einem der vorhergehenden Ansprüche, die eine dimere Struktur hat.
- 10 11. Metallocenverbindung nach einem der vorhergehenden Ansprüche, umfassend (t-Butylamido)(2-methyl-4,5-benzoiden-1-yl)-1,1-dimethylsilanzirconiumchlorid oder (t-Butylamido)(2-methyl-4,5-benzoiden-1-yl)-1,1-dimethylsilantitanchlorid.
12. Katalysatorsystem für Verwendung beim Herstellen von Polyolefinen, das umfaßt (a) eine Metallocenverbindung, wie in einem der vorhergehenden Ansprüche definiert, und (b) einen Aluminium oder Bor enthaltenden Cokatalysator, fähig zum Aktivieren der Metallocenverbindung.
- 15 13. Katalysatorsystem nach Anspruch 12, das ferner einen inerten Träger umfaßt.
14. Verwendung einer Metallocenverbindung oder eines Katalysatorsystems, wie in einem der vorhergehenden Ansprüche definiert, als eine Katalysatorkomponente für die Herstellung eines Polyolefins.
- 20 15. Verwendung nach einem von Ansprüchen 12-14, wobei das Polyolefin isotaktisches Polypropylen umfaßt.
16. Verfahren zum Herstellen von Polyolefinen, das umfaßt in Kontakt bringen eines Katalysatorsystems, wie in Anspruch 12 oder Anspruch 13 definiert, mit mindestens einem Olefin in einer Reaktionszone unter Polymerisationsbedingungen.
- 25 17. Verfahren nach Anspruch 16, wobei das Olefin Propylen ist, und das Polyolefin ist isotaktisches Polypropylen.
- 30 18. Verwendung einer Metallocenverbindung als eine Katalysatorkomponente für die Herstellung von isotaktischem Polypropylen, wobei die Metallocenverbindung ein Metallocen mit der allgemeinen Formel:  $\text{CpAXMQ}_1\text{Q}_2\text{Cp}'\text{A}'\text{X}'\text{M}'\text{Q}'_1\text{Q}'_2$  umfaßt, wobei Cp und Cp' jeweils unabhängig ein substituierter oder unsubstituierter Cyclopentadienylrest sind; M und M' sind jeweils unabhängig ein Metall, ausgewählt aus Gruppe IVB Übergangsmetallen und Vanadium, und koordinieren an Cp bzw. Cp'; X und X' sind jeweils unabhängig ein substituiertes oder unsubstituiertes Gruppe VA oder VIA Heteroatom und koordinieren an M bzw. M'; A und A' sind Verbrückungsgruppen zwischen Cp und X und zwischen Cp' und X' und sind unabhängig aus  $-\text{SiR}'_2\text{-O-SiR}'_2$ ,  $-\text{Si}_n\text{R}'_m$ ,  $-\text{C}_n\text{R}'_m$  und  $-\text{CR}'_2\text{-SiR}'_2\text{-CR}'_2\text{-SiR}'_2$  ausgewählt, wobei jedes R' unabhängig H oder Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen ist, n ist eine ganze Zahl in dem Bereich von 1 bis 4, und  $m=2n$ ; jedes Q<sub>1</sub>, Q<sub>2</sub> und Q<sub>1</sub>' und Q<sub>2</sub>' ist unabhängig eine Koordinierungsgruppe, die Wasserstoff, Halogen oder Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen ist, und jedes von Q<sub>1</sub> and Q<sub>1</sub>' ist an beide M und M' koordiniert.
- 35 36 40 19. Verwendung nach Anspruch 18, wobei die Metallocenverbindung eine Verbindung, wie in einem von Ansprüchen 1-11 definiert, umfaßt.
- 45 20. Verwendung eines Katalysatorsystems zum Herstellen von isotaktischem Polypropylen, wobei das System umfaßt (a) eine Metallocenverbindung, wie in Anspruch 18 oder Anspruch 19 definiert, und (b) einen Aluminium oder Bor enthaltenden Cokatalysator, fähig zum Aktivieren der Metallocenverbindung.
- 50 21. Verfahren zum Herstellen von isotaktischem Polypropylen, das umfaßt in Kontakt bringen eines Katalysatorsystems, wie in Anspruch 20 definiert, mit Propylen in einer Reaktionszone unter Polymerisationsbedingungen.
- 55 22. Verwendung eines Katalysators, umfassend eine Metallocenverbindung für die Herstellung von isotaktischem Polypropylen, wobei die Metallocenverbindung die allgemeine Formel  $\text{CpAXMQ}_2$  hat, in der Cp ein substituierter Cyclopentadienylrest ist; M ist ein Metall, ausgewählt aus Gruppe IVB Übergangsmetallen und Vanadium, und koordiniert an Cp; X ist ein substituiertes oder unsubstituiertes Gruppe VA oder VIA Heteroatom, das an M koordiniert; A ist eine Verbrückungsgruppe zwischen Cp und X, die aus  $-\text{SiR}'_2\text{-O-SiR}'_2$ ,  $-\text{Si}_n\text{R}'_m$ ,  $-\text{C}_n\text{R}'_m$  und  $-\text{CR}'_2\text{-SiR}'_2\text{-CR}'_2\text{-SiR}'_2$  ausgewählt ist, wobei jedes R unabhängig H oder Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen ist, n ist eine ganze Zahl in dem Bereich von 1 bis 4 und  $m=2n$ ; und jedes Q ist unabhängig Wasserstoff, Halogen

oder Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen.

23. Verwendung nach Anspruch 22, wobei der Cyclopentadienylrest ein substituiertes Indenyl ist.

5 24. Verwendung nach Anspruch 23, wobei der substituierte Indenylrest substituiertes Benzoidenyl ist.

25. Verwendung nach einem von Ansprüchen 22 bis 24, wobei der Cyclopentadienylrest an Position 2 substituiert ist.

10 26. Verwendung nach Anspruch 25, wobei der Cyclopentadienylrest mit einem Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen substituiert ist.

27. Verwendung nach einem von Ansprüchen 22 bis 26, wobei das Metall Zr ist.

15 28. Verwendung nach einem von Ansprüchen 22 bis 27, wobei das Heteroatom Stickstoff, Phosphor, Sauerstoff oder Schwefel ist und mit H, Hydrocarbyl mit 1 bis 20 Kohlenstoffatomen oder Silyl substituiert ist.

29. Verwendung nach Anspruch 28, wobei das Heteroatom Stickstoff ist.

20 30. Verwendung nach einem von Ansprüchen 22 bis 29, wobei A  $\text{SiR}'_2$  ist.

31. Verwendung nach Anspruch 30, wobei jedes R' Methyl ist.

25 32. Verwendung nach einem von Ansprüchen 22 bis 31, wobei der Katalysator ferner einen Aluminium oder Bor enthaltenden Cokatalysator, fähig zum Aktivieren der Metallocenverbindung, umfaßt.

33. Verwendung nach einem von Ansprüchen 22 bis 32, wobei die Metallocenverbindung aus einer Metallocenverbindung, wie in einem von Ansprüchen 1 bis 11 definiert, gebildet ist.

30 **Revendications**

35 1. Un composé de métallocène ayant la formule générale:  $\text{CpAXMQ}_1\text{Q}_2\text{Cp}'\text{A}'\text{X}'\text{M}'\text{Q}'_1\text{Q}'_2$  où Cp et Cp' sont chacun indépendamment un résidu indényle substitué ou non substitué; M et M' sont chacun indépendamment un métal choisi dans le groupe IVB des métaux de transition et le vanadium, et coordonnés à un Cp et Cp' respectivement; X et X' sont chacun indépendamment un hétéroatome du groupe VA ou VIA substitué ou non substitué et coordonnés à M et M' respectivement; A et A' sont des groupes de pontage entre Cp et X et entre Cp' et X' respectivement et sont chacun choisis indépendamment parmi  $-\text{SiR}'_2-\text{O}-\text{SiR}'_2-$ ,  $-\text{Si}_n\text{R}'_m-$ ,  $-\text{C}_n\text{R}'_m-$  et  $-\text{CR}'_2-\text{SiR}'_2-\text{CR}'_2-\text{SiR}'_2-$ , où chaque R' est indépendamment H ou un hydrocarbyle ayant de 1 à 20 atomes de carbone, n est nombre entier dans l'intervalle de 1 à 4 et  $m=2n$ ; chacun des  $\text{Q}_1$ ,  $\text{Q}_2$  et  $\text{Q}'_1$  et  $\text{Q}'_2$  sont indépendamment un groupe de coordination qui est l'hydrogène, un halogène ou un hydrocarbyle ayant 1 à 20 atomes de carbone et chaque  $\text{Q}_1$  et  $\text{Q}'_1$  est coordonné avec à la fois M et M'.

45 2. Un composé de métallocène selon la revendication 1 où chaque résidu indényle est un benzoidényle substitué ou non substitué.

3. Un composé de métallocène selon la revendication 1 ou la revendication 2 où le résidu indényle est substitué en position 2 avec un hydrocarbyle ayant de 1 à 20 atomes de carbone.

50 4. Un composé de métallocène selon l'une quelconque des revendications précédentes où le métal est Zr.

5. Un composé de métallocène selon l'une quelconque des revendications précédentes où le hétéroatome est l'azote, le phosphore, l'oxygène ou le soufre et est substitué par un H, un hydrocarbyle ayant de 1 à 20 atomes de carbone ou silyle.

55 6. Un composé de métallocène selon la revendication 5 où l'hétéroatome est l'azote.

7. Un composé de métallocène selon l'une quelconque des revendications précédentes où chaque A et A' est un  $\text{SiR}'_2$ .

8. Un composé de métallocène selon la revendication 7 où chaque R' est un méthyle.
9. Un composé de métallocène selon l'une quelconque des revendications précédentes dont le site actif a une symétrie C2 locale.
- 5 10. Un composé de métallocène selon l'une quelconque des revendications précédentes qui a une structure dimère.
11. Un composé de métallocène selon l'une quelconque des revendications précédentes comprenant du chlorure de (t-butylamido)(2-méthyl-4,5-benzoindèn-1-yl)-1,1-diméthyle silane zirconium ou du chlorure de (t-butylamido)  
10 (2-méthyl-4,5-benzoindèn-1-yl)-1,1-diméthyl silane titane.
12. Un système de catalyseur à utiliser pour la préparation de polyoléfines qui comprend (a) un composé de métallocène comme défini dans l'une quelconque des revendications précédentes; et (b) un co-catalyseur contenant de l'aluminium ou du bore capable d'activer le composé de métallocène.
- 15 13. Un système de catalyseur selon la revendication 12 qui comprend, en outre, un support inerte.
14. Utilisation d'un composé de métallocène ou d'un système de catalyseur comme défini dans l'une quelconque des revendications précédentes comme composant de catalyseur pour la production d'une polyoléfine.
- 20 15. Utilisation selon l'une quelconque des revendications 12 à 14, où la polyoléfine comprend un polypropylène isotactique.
16. Procédé pour la préparation de polyoléfines, qui comprend la mise en contact d'un système de catalyseur tel que défini dans les revendications 12 ou 13 avec au moins une oléfine dans une zone de réaction sous des conditions de polymérisation.
- 25 17. Un procédé selon la revendication 16, où l'oléfin est le propylène et la polyoléfine est un polypropylène isotactique.
- 30 18. Utilisation d'un composé de métallocène comme composant de catalyseur pour la production d'un polypropylène isotactique, où le composé de métallocène comprend un métallocène ayant la formule générale:  $CpAXMQ_1Q_2Cp'A'X'M'Q_1'Q_2'$  où Cp et Cp' sont chacun indépendamment un résidu de cyclopentadiényle substitué ou non substitué; M et M' sont chacun indépendamment un métal choisi dans le groupe IVB des métaux de transition et le vanadium, et coordonnés à un Cp et Cp' respectivement; X et X' sont chacun indépendamment un hétéroatome des groupes VA ou VIA substitué ou non substitué et coordonnés à M et M' respectivement; A et A' sont des groupes de pontage entre Cp et X et entre Cp' et X' respectivement et sont chacun choisis indépendamment parmi  $-SiR'_2-O-SiR'_2-$ ,  $-Si_nR'_m-$ ,  $-C_nR'_m-$  et  $-CR'_2-SiR'_2-CR'_2-SiR'_2-$ , où chaque R' est indépendamment H ou un hydrocarbyle ayant de 1 à 20 atomes de carbone, n est nombre entier dans l'intervalle de 1 à 4 et  $m=2n$ ; chacun des Q<sub>1</sub>, Q<sub>2</sub> et Q<sub>1</sub>' et Q<sub>2</sub>' sont indépendamment un groupe de coordination qui est l'hydrogène, un halogène ou un hydrocarbyle ayant de 1 à 20 atomes de carbone et chaque Q<sub>1</sub> et Q<sub>1</sub>' est coordonné avec à la fois M et M'.
- 35 40 19. Utilisation selon la revendication 18 où le composé de métallocène comprend un composé défini dans l'une quelconque des revendications 1 à 11.
- 45 20. Utilisation d'un système de catalyseur pour préparer un polypropylène isotactique qui comprend (a) un composé de métallocène tel que défini dans la revendication 18 ou la revendication 19; et (b) un co-catalyseur contenant de l'aluminium ou du bore capable d'activer le composé de métallocène.
- 50 21. Procédé pour préparer un polypropylène isotactique qui comprend mettre en contact un système de catalyseur tel que défini dans la revendication 20 avec du propylène dans une zone de réaction sous des conditions de polymérisation.
- 55 22. Utilisation d'un catalyseur comprenant un composé de métallocène pour la production d'un polypropylène isotactique, où le composé de métallocène a la formule générale:  $CpAXMQ_2$  où Cp est un résidu cyclopentadiényle substitué, M est un métal choisi dans le groupe IVB des métaux de transition et le vanadium, et se coordonne au Cp; X est un hétéroatome du groupe VA ou VIA substitué ou non substitué et qui se coordonne à M; A est un groupe de pontage entre Cp et X qui est choisi parmi  $-SiR'_2-O-SiR'_2-$ ,  $-Si_nR'_m-$ ,  $-C_nR'_m-$  et  $-CR'_2-SiR'_2-CR'_2-SiR'_2-$ , où chaque R' est indépendamment H ou un hydrocarbyle ayant de 1 à 20 atomes de carbone, n est nombre entier

## EP 1 153 032 B1

dans l'intervalle de 1 à 4 et  $m=2n$ ; chaque Q est indépendamment l'hydrogène, un halogène ou un hydrocarbyle ayant 1 à 20 atomes de carbone.

- 5
23. Utilisation selon la revendication 22, où le résidu cyclopentadiényle est une indényle substitué.
24. Utilisation selon la revendication 23 où le résidu indényle substitué est un benzoindényle substitué.
- 10
25. Utilisation selon l'une quelconque des revendications 22 à 24 où le résidu cyclopentadiényle est substitué en position 2.
26. Utilisation selon la revendication 25 où le résidu cyclopentadiényle est substitué par un hydrocarbyle ayant de 1 à 20 atomes de carbone.
- 15
27. Utilisation selon l'une quelconque des revendications 22 à 26 où le métal est Zr.
28. Utilisation selon l'une quelconque des revendications 22 à 27 où le hétéroatome est l'azote, le phosphore, l'oxygène ou le soufre et est substitué par un H, hydrocarbyle ayant de 1 à 20 atomes de carbone ou silyle.
- 20
29. Utilisation selon la revendication 28 où l'hétéroatome est l'azote.
30. Utilisation selon l'une quelconque des revendications 22 à 29 où A est  $\text{SiR}'_2$ .
31. Utilisation selon la revendication 30 où chaque R' est un méthyle.
- 25
32. Utilisation selon l'une quelconque des revendications 22 à 31 où le catalyseur comprend, en outre, un co-catalyseur contenant de l'aluminium ou du bore capable d'activer le composé de métallocène.
- 30
33. Utilisation selon l'une quelconque des revendications 22 à 32 où le composé de métallocène est formé à partir d'un composé de métallocène tel que défini selon l'une quelconque des revendications 1 à 11.

35

40

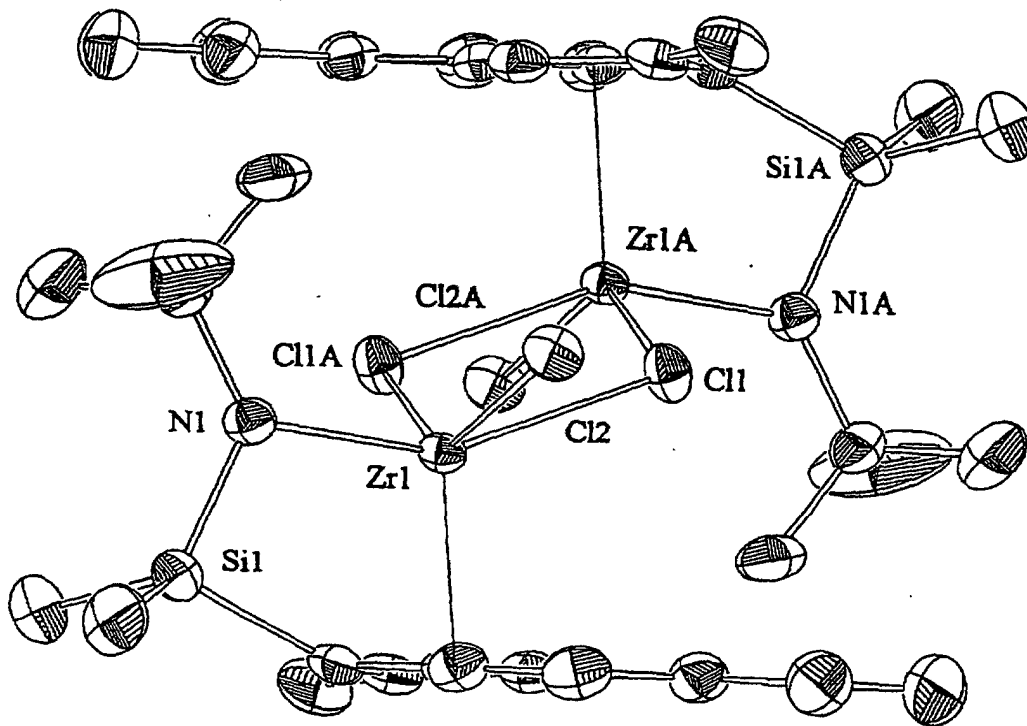
45

50

55

FIG . 1

Crystal Structure Analysis for  
 $(\text{Me}_2\text{Si}(\text{tbut N})(2\text{-MeBenzInd})\text{ZrCl}_2)_2$



**FIGURE 2**  
**13 C NMR SPECTRUM OF THE POLYMER**

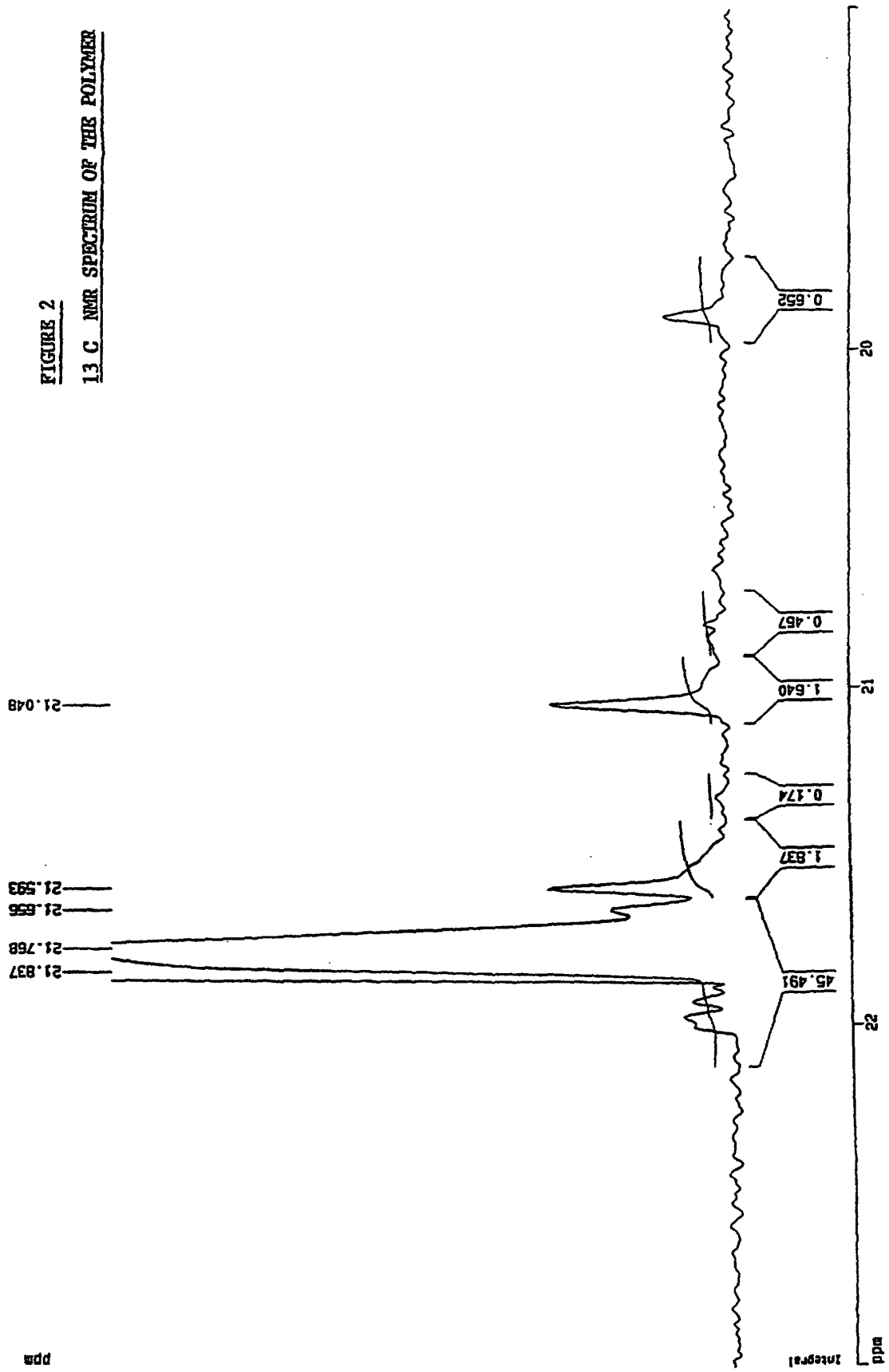




FIGURE 3  
1 HMR SPECTRUM OF THE METALLOCENE IN CO<sub>2</sub>Cl<sub>2</sub> AT 25°C

